High solids content nitroxide mediated miniemulsion polymerization of n-butyl methacrylate

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The synthesis of poly(*n*-butyl methacrylate) by nitroxide mediated miniemulsion polymerization is described using the alkoxyamine 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile. Polymerizations are successfully conducted to high conversions with high solids content (up to 52 %) and molecular weight up to 60,000 g/mol, whilst maintaining reasonable control of the reaction. It is shown that by performing the polymerization in aqueous media, problems that arise when targeting high molecular weights in bulk/solution due to build-up of nitroxide can be overcome. The ability to chain extend the resulting polymers is demonstrated and opens the possibility for synthesis of a wide range of macromolecular structures in dispersed media.

Introduction

The polymerization of methacrylic monomers by nitroxide mediated polymerization (NMP) has been a long standing challenge.[1,2] Whilst styrene and acrylates can be used in NMP with relatively few complications,[3] in the NMP of methacrylates, disproportionation between the propagating chain end and the nitroxide often occurs, leading to terminally unsaturated chains.[4–7] The early work on NMP of methacrylates conducted at CSIRO also showed that with methacrylic monomers the equilibrium constant tends to be higher than for styrene and acrylic monomers, which leads to relatively high rates of termination and loss of control of the reaction.[8,9] One technique which is now commonly applied to overcome this problem, is to copolymerize methacrylates with a small amount of a second monomer (for example styrene), which lowers the effective equilibrium constant and reduces the concentration of radicals, such that the polymerization can be conducted without excessive termination.[10–13]

A number of nitroxides/alkoxyamines have been reported which are able to overcome the issues that are typically present in the NMP of methacrylates, without the need for addition of comonomers.[14–17] The synthesis of these molecules tends to be laborious and/or expensive which puts a limit on the feasibility of using such regulators on a large scale. By contrast, we recently presented a series of alkoxyamines, which are synthesized in an easy and cost-effective manner and are capable of effectively controlling solution polymerization of methacrylates at temperatures below 100 °C.[18,19] While the molecular weight at the beginning of the reaction was higher than the theoretically expected, polymers with controlled molecular weight and moderate dispersity were obtained. The low temperature at which these reactions were conducted is

particularly useful as it opens the possibility for NMP of methacrylates in dispersed aqueous media, which is the subject of the present work.

Polymerization in aqueous media presents a number of advantages over synthesis in solution, especially with regards to the cost and environmentally friendly nature of using water as solvent.[20–22] However, in reversible deactivation radical polymerizations (RDRP), and in NMP in particular, these advantages come with a number of drawbacks.[23–25] The heterogeneous nature of dispersed phase polymerizations results in partitioning of the reactants and can lead to difficulties in controlling the polymerization. This is especially the case in emulsion polymerization, which is dependent on transport of components through the aqueous phase. For this reason, miniemulsion polymerization is commonly used with RDRPs conducted in dispersed media, which alleviates the need for transport of the control agent through the aqueous phase and, therefore, similar formulations as those used in bulk can be applied. Specifically for NMP, partitioning of the nitroxide into the aqueous phase can be a significant problem since many nitroxides undergo rapid decomposition in aqueous media at low pH, resulting in a loss of control of the reaction.[26] It is worth pointing out that despite its apparent simplicity, miniemulsification is the bottleneck for industrialization of miniemulsion polymerization[27] and that high pressure homogenizers are a promising route for conducting miniemulsification on a large scale.[28]

The compartmentalized nature of polymerizations conducted in dispersed media can also result in marked differences in the rate of polymerization and control over the polymerization in RDRP systems which operate on the basis of the persistent radical effect, compared to the analogous reactions conducted in bulk/solution.[29–31] These differences are related to: (1) a decrease in the rate of bimolecular termination between propagating radicals due to segregation of the propagating radicals in distinct particles, and (2) an increase in the rate of radical deactivation due to the confined space in which the nitroxide and propagating radicals are contained. These effects typically become important at particle sizes below 100 nm and numerous experimental works and simulations have shown the

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importance of the interplay between reduced termination and increased rates of recombination.[32–37]

In the literature two main NMP systems exist which have been utilized in miniemulsion polymerization: (1) the (2,2,6,6-tetra-methylpiperidin-1-yl)oxyl (TEMPO) mediated polymerization of styrene and (2) N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)nitroxide] (SG1) based systems. Due to the low equilibrium constant of the TEMPO-styrene system these reactions are typically slow and are therefore conducted at high temperatures (T > 120 °C) which require the use of pressurized vessels,[32,38–40] although there are a few reports of temperatures around 100 °C being used with the addition of nitroxide scavengers.[41,42] In the second case, SG1 based systems have widely been used to polymerize both styrene and acrylic monomers either using an SG1-based alkoxyamine such as BlocBuilder at 112 °C (acrylates) or 120 °C (styrene),[26,43] or using SG1 in combination with a radical source such as AIBN or potassium persulfate at 90 °C.[26,44,45] In the latter case, the reactions can be performed at atmospheric pressure, but molecular weight distributions are typically broader. These reactions tend to be conducted at around 20 % solids content, due to the known issues regarding the stability of dispersed phase polymerizations in RDRP,[46] although there are a few reports using up to around 45 % solids content by multistep/semi-batch procedures.[47–49]

The homopolymerization of methacrylates in dispersed media by NMP has not been reported due to the known issue of nitroxide disproportionation, but there have been some publications utilizing the copolymerization strategy.[47,50–54] For example. Dire *et al.* utilized a poly(methacrylic acid) based macroalkoxyamine in the surfactant free emulsion polymerization of methyl methacrylate using styrene as comonomomer.[50] In the absence of comonomer a limiting conversion of around 70 % was obtained, while no control over the molecular weight was observed.

In this article, we present results on the miniemulsion polymerization of butyl methacrylate using 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (see Scheme 1). First, the potential for synthesis of polymers of a wide range of molecular weights is demonstrated. For moderate degrees of polymerization, the polymerization proceeds with similar rates and with similar control over molecular weight compared to the corresponding system in bulk. It is shown that when targeting higher degrees of polymerization, miniemulsion polymerization is capable of overcoming the limited conversion observed in bulk polymerization. Stable polymer dispersions were obtained with solids content up to 52 %, which represents the upper limit of previous reports of RDRP in dispersed systems, without any adverse effects on the control of the polymerization. Finally, we report the potential to synthesize block copolymers, thus demonstrating the potential to produce complex macromolecular architectures in aqueous media.
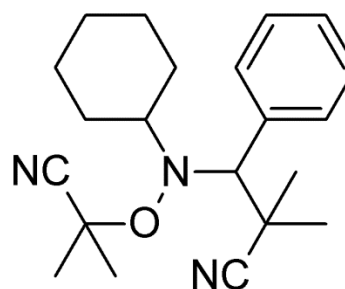
Scheme 1 Structure of 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile.

Experimental Section

Materials

n-Butyl methacrylate (BMA, Aldrich, 99%), stearyl methacrylate (SMA, Aldrich, mixture of stearyl and cetyl methacrylates), benzyl methacrylate (BzMA, Aldrich, 96%), 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, Wako), Dowfax 2A1 (alkyl diphenyloxide disulfonate, 45 wt% active content, Dow Chemical) and L-ascorbic acid (AsA, Aldrich, 99%) were used as received. 3-(((2-cyanopropan-2-yl)oxy)-(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile was synthesized according to a previously published procedure.[18] All solvents were purchased from Scharlab, were of technical grade, and were used without purification.

Methods

Z-average particle diameters were determined by dynamic light scattering performed on a Malvern Zetasizer ZS using a scattering angle of 173° at a standard temperature of 25 °C. Molecular weight distributions of polymers were measured by size exclusion chromatography (SEC). Samples were dried and diluted in THF (HPLC grade) to a concentration of approximately 5 mg.mL^{-1} and filtered through a 0.45-μm nylon filter. The SEC set up consisted of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6 with pore sizes ranging from 10^2 to 10^6 Å). Chromatograms were obtained in THF (HPLC grade) at 35 °C using a flow rate of 1 mL.min^{-1}. The equipment was calibrated using narrow polystyrene standards ranging from 595 to 3.95×10^6 Da (5th order universal calibration). The molecular weight was determined using the Mark-Houwink parameters of K = 1.14×10^{-5} L/g, α = 0.716 for polystyrene and K = 1.48×10^{-5} L/g and α = 0.664 for poly(butyl methacrylate).[55] Conversions were determined gravimetrically. The stability of the miniemulsions was determined by means of a Turbiscan Lab Expert. Latex viscosity was measured using an A&D SV-10 viscometer at a temperature of 25 °C.

Miniemulsion Polymerization

Miniemulsion polymerizations were carried out in 100-mL stainless-steel stirred reactors (Miniplant, Chemspeed Technologies). In a typical reaction, stearyl methacrylate (acting as costabilizer) (1.2 g) and 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (0.19 g, 0.56 mmol) were dissolved in BMA (16 g, 0.11 mol). The

organic phase was added to a stirred solution of Dowfax 2A1 (0.8 g) in water (64 g). The coarse emulsion was stirred for 10 minutes. The resulting emulsion was sonicated using a Branson 450 sonifier operating at 70% output control and 0.5 duty cycle for 5 min in an ice bath and under magnetic stirring.

Table 1 Recipes for synthesis of poly(n-butyl methacrylate) by nitroxide mediated miniemulsion polymerization at 90 °C.

Run	solids content (%)	target Mn (kg/mol)	organic phase			aqueous phase	
			n-butyl methacrylate (g)	stearyl methacrylate (g)	alkoxyamine (g)	water (g)	Dowfax 2A1 (g)
1	-	30.8	32	2.40	0.38	-	-
2	21	30.8	16	1.20	0.19	64	0.16
3	21	30.8	16	1.20	0.19	64	0.80
4	21	30.8	16	1.20	0.19	64	1.60
5	21	15.7	16	1.20	0.38	64	0.80
6	21	61.4	16	1.20	0.09	64	0.80
7	42	30.8	32	2.40	0.38	48	1.60
8	52	30.8	40	3.00	0.48	40	2.00
9[a]	21	61.4	16	1.20	0.09	64	0.80
10[b]	21	61.4	16	1.20	0.09	64	0.80
11[c]	21	61.4	16	1.20	0.09	64	0.80

[a] Run 9 conducted with additional 0.020 g VA-086 ([VA-086] / [Alkoxyamine] = 0.25).

[b] Run 10 conducted with continuous addition of an aqueous solution of L-ascorbic acid (1.65 mg/mL) at a rate of 0.02 mL/min ([AsA] / [Alkoxyamine] = 0.25).

[c] Run 11 was acidified to pH 4.7 using 1 M HCl after preparation of the miniemulsion.

The resulting miniemulsion was added to the stainless steel reactor and subsequently bubbled with nitrogen for 20 minutes. The reactions were heated to 90 °C over 10 minutes and maintained at a constant stirring rate of 150 rpm. Samples (≈ 2 mL) were taken periodically for measurement of molecular weight and conversion.

The miniemulsion homopolymerizations of BMA performed are given in Table 1. Run 1 is a comparative bulk polymerization. Runs 2 to 4 investigate the effect of surfactant concentration ranging from 0.45 wt % based on monomer (wbm) to 4.5 wbm, Runs 3, 5 and 6 the effect of alkoxyamine concentration and Runs 3, 7 and 8 the effect of solids content. In Runs 9 to 11 the potential for the synthesis of higher molecular weight polymers using miniemulsion was explored.

Chain extension experiments

A 10 wt% poly(n-butyl methacrylate) seed latex was synthesized by batch miniemulsion polymerization using the recipe in Table 2 by a similar procedure as that described above with the exception that the reaction was performed for 5 h at 87 °C in a 500 mL double walled glass reactor equipped with anchor type stirrer, nitrogen inlet, condenser and thermocouple (X = 0.88, M_n = 37700 g/mol, $Đ$ = 1.47, $\overline{D}_z$ = 159 nm). Chain extension reactions were carried out in 100-mL stainless-steel stirred reactors (Miniplant, Chemspeed Technologies). The seed latex (50 g) was charged to the reactor and bubbled with nitrogen for 20 minutes. The reactor was heated to 90 °C and benzyl methacrylate (5 g, BMA:BzMA = 1:1 weight ratio) was added as a single shot. After 5 h the reaction was cooled to room temperature.

Table 2 Recipe for synthesis of seed poly(n-butyl methacrylate) with DP$_n$ = 200 by nitroxide mediated miniemulsion polymerization at 87 °C.

	weight (g)
n-butyl methacrylate	32
stearyl methacrylate	2.40
alkoxyamine	0.38
water	288
Dowfax 2A1	1.6

Results

A series of miniemulsion polymerizations of n-butyl methacrylate were conducted using stearyl methacrylate as reactive costabilizer and varying quantities of Dowfax 2A1 as surfactant with a solids content of 21 wt% (Runs 2-4). A comparative bulk polymerization (Run 1) was performed in order to evaluate the effect of conducting the polymerization in dispersed media. In all cases, a similar polymerization rate was achieved and high conversion (X > 0.8) was reached within 6 hours (see Figure 1). The initial droplet size decreased with increasing surfactant concentration and remained almost

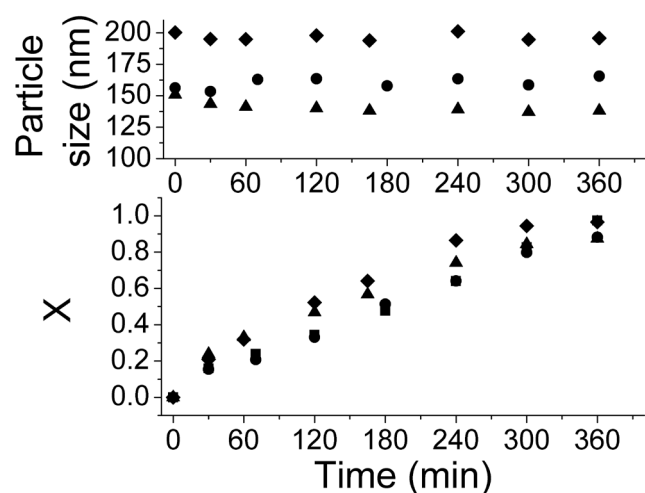constant during the reactions in all cases, indicating efficient droplet nucleation.

Figure 1 Effect of surfactant concentration on kinetics of polymerization (bottom) and the evolution of *z*-average particle size (top) in miniemulsion polymerization of BMA. Bulk polymerization (Run 1, squares), 0.45 wbm Dowfax (Run 2, diamonds), 2.25 wbm Dowfax (Run 3, circles) and 4.5 wbm Dowfax. (Run 4, triangles). [BMA] / [AAm] = 200.

The evolution of molecular weight with conversion was linear in all cases, and the dispersity of the final polymers were also similar (Đ ≈ 1.4) (see Figure 2). In agreement with previous studies in bulk and solution, which showed that comparatively slow initiation as a result of a strong penultimate effect leads to an initial overshoot in the molecular weight,[18] the number average molecular weight was consistently above the theoretical line. The effect is stronger here than was previously observed in solution,[18,19] since both in miniemulsion and bulk polymerization the local monomer concentration is higher than in solution. At high conversions, the theoretical molecular weight is approached but the fact that molecular weight remains higher than the theoretical line suggests the initiator efficiency is not 100 %, likely as a result of the relatively fast polymerization compared to the timescale required for complete alkoxyamine decomposition. In contrast, previous batch[18] and semi-batch[19] reactions in solution, where reaction times are significantly longer but the timescale for alkoxyamine decomposition is the same, have shown the theoretical line is approached at lower conversions. Slow initiation relative to the overall polymerization rate is also evidenced by a low molecular weight tail in the molecular weight distributions, which could be seen in both reactions run in bulk and in miniemulsion (see Figure S1), and in the appearance of an acceleration in the first-order kinetic plot in all cases (see Figure S2).

The negligible differences in the rate of polymerization and evolution of molecular weight between the different samples indicate that the particle size was not small enough (d >130 nm) for any effects of compartmentalization to be observed, even at the largest surfactant concentrations used. It has previously been shown that for a system in which the equilibrium is shifted significantly to the dormant state, the effect of particle diameter is negligible where d > ≈100 nm since above this

threshold the local concentration of radicals and nitroxide species approaches that of the bulk case.[34]
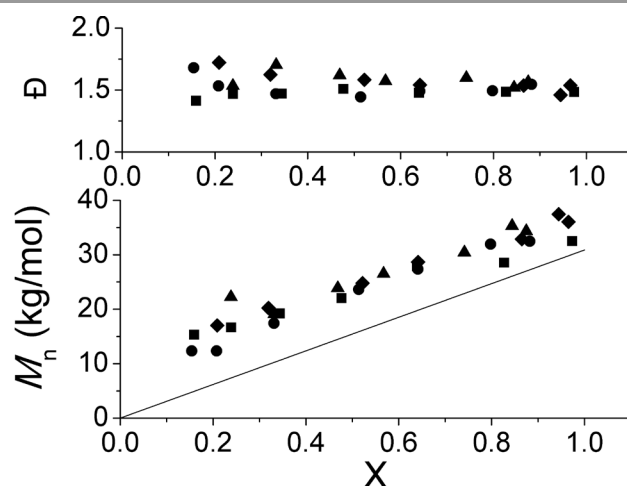

Figure 2 Effect of surfactant concentration on the evolution of molecular weight and dispersity in miniemulsion polymerization of BMA. Bulk polymerization (Run 1, squares), 0.45 wbm Dowfax (Run 2, diamonds), 2.25 wbm Dowfax (Run 3, circles) and 4.5 wbm Dowfax. (Run 4, triangles). [BMA] / [AAm] = 200.

The concentration of alkoxyamine was varied to evaluate the degree of control possible when targeting higher or lower molecular weights (Runs 3, 5 and 6). The polymerization kinetics and the evolution of molecular weight with conversion are shown in Figure 3. When the alkoxyamine concentration was increased, the reaction proceeded at a faster rate as may be expected due to the higher radical concentration, the increase being approximately proportional to the increase in alkoxyamine concentration (see Figure S3). The increase in the alkoxyamine concentration also led to a reduction in the molecular weight, in line with what is expected for a controlled polymerization, although the molecular weight was above the theoretical value. In the case of the lowest target molecular weight (Run 5), this is particularly visible due to the fast rate of polymerization relative to initiation. This results in a higher percentage of the starting alkoxyamine remaining uninitiated at high conversion, leading to higher molecular weight than would be expected assuming 100 % initiator efficiency.

When targeting higher molecular weights, although the molecular weight evolved linearly with conversion, the reaction slowed significantly around X = 0.4 as can be seen in the first-order kinetics plot (see Figure S3). This has also previously been observed in the solution polymerization of methyl methacrylate using the same alkoxyamine.[18] This strong decrease in the polymerization rate may occur as a result of several issues. Firstly, the build-up of nitroxide, as a result of bimolecular termination between propagating radicals, would lead to a shift in the equilibrium such that the polymerization is effectively stopped, as has been reported in the TEMPO mediated polymerization of acrylates.[56] Secondly, partitioning of the nitroxide into the aqueous phase, which leads to an initial reduction in the local nitroxide concentration in the polymerizing particles, may lead to an enhanced degree of termination and further aggravate this problem.[57,58] However,

partitioning is not thought to play a major role since similar observations of slow rates, which appear to level off at low conversion (X < 0.5) have previously been observed in solution polymerization of MMA with the same alkoxyamine.[18] Finally, in addition to these conventional bimolecular termination reactions, methacrylic monomers are prone to an additional disproportionation reaction in NMP.[1] This reaction generates a terminally unsaturated chain and a hydroxylamine, and would lead to a reduction in the rate of polymerization, although for the present alkoxyamine this effect is expected to be significantly reduced.[18]
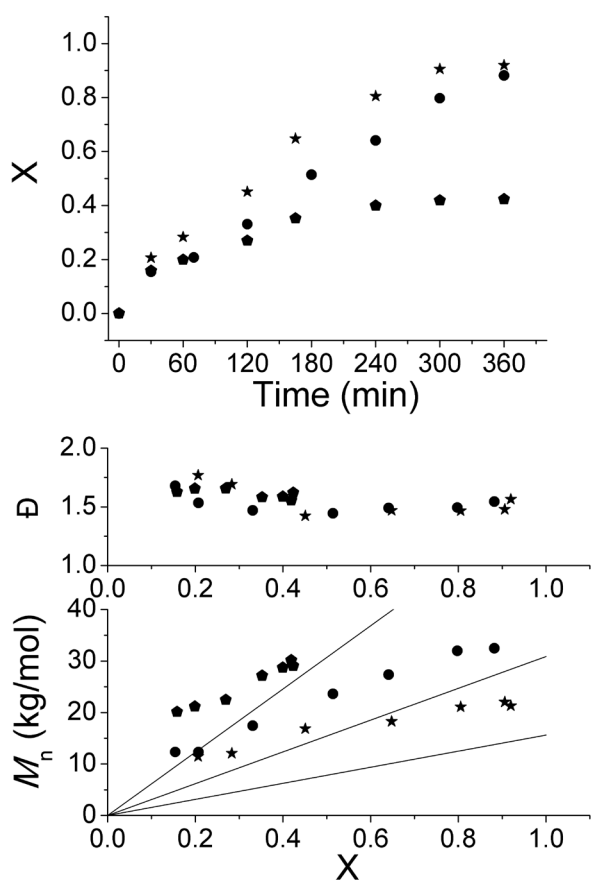
400. In the presence of additional radical initiator (VA-086, Run 9) polymerization proceeded to high conversion and the molecular weight increased with increasing conversion. However, the molecular weight was substantially lower than may be expected taking into account [BMA]/[alkoxyamine] ratio and the dispersity was high (Đ > 2) throughout the reaction. In the presence of ascorbic acid (Run 10), high conversion was achieved and molecular weight evolved linearly with conversion, with Đ ≈ 1.8. When the reaction was conducted at low pH (Run 11) conversion was also relatively high and an increase of molecular weight with conversion was observed, with Đ ≈ 1.6.

These results suggest that the cause of the slow polymerization rate at high target molecular weights is a build-up of nitroxide radicals due to conventional termination reactions. The addition of a radical initiator generates new radicals which reduces the build-up of nitroxide, thus resulting in a reasonable rate of reaction. However, the generation of new radicals results in a lower molecular weight compared to what may be expected assuming all chains are initiated from the alkoxyamine and also leads to a number of dead chains which is observed experimentally through the high dispersity. Addition of ascorbic acid reduces the nitroxide radical concentration by scavenging nitroxide in the aqueous phase, thus resulting in a higher rate of polymerization, although the low nitroxide concentration also reduces control of the polymerization and leads to a slightly higher dispersity than is typical for this alkoxyamine. At low pH, nitroxide in the aqueous phase can be decomposed by disproportionation[26,59] and thus reasonable rates of polymerization are observed in this case as well. Therefore, the reduction in the rate of polymerization in the absence of additives was related to a build-up of nitroxide, rather than a result of chain termination by disproportionation of the propagating radical with nitroxide. This was further supported by an additional experiment which involved addition of the ascorbic acid after the rate of polymerization had dropped off and resulted in a rapid increase in conversion (see Figure S4).
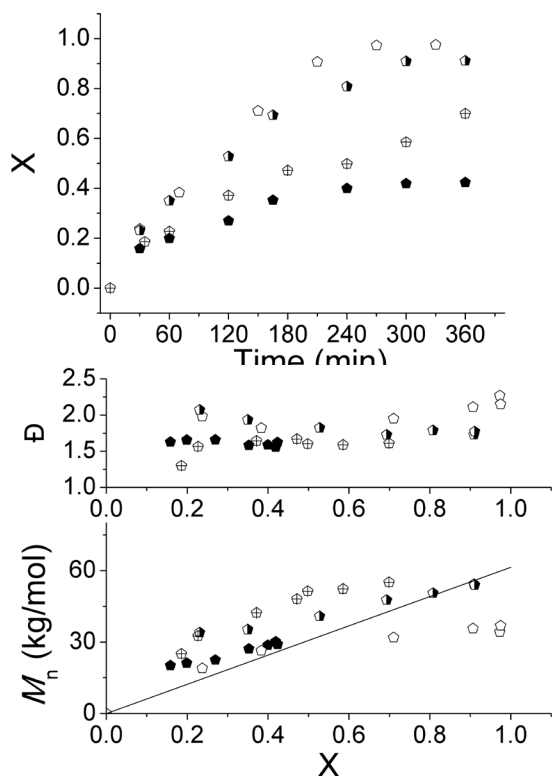

Figure 3 Effect of alkoxyamine concentration on kinetics of miniemulsion polymerization of BMA (top) and evolution of molecular weight and dispersity with conversion (bottom). [BMA] / [AAm] = 100 (Run 5, stars), [BMA] / [AAm] = 200 (Run 3, circles) and [BMA] / [AAm] = 400 (Run 6, pentagons).

In order to investigate the cause of the sluggish polymerization when targeting higher molecular weights, additional reactions were performed in the presence of; (1) an additional radical source in the form of a water soluble azo-initiator (VA-086, Run 9), (2) with continuous addition of a water soluble nitroxide scavenger[41,56] (ascorbic acid, Run 10), and (3) with the reaction medium acidified to pH 4.7 prior to polymerization (Run 11). Figure 4 shows the kinetics and the evolution of molecular weight with conversion of the reactions with a target DP_n of

Figure 4 Effect of addition of external initiating source and nitroxide scavenger on kinetics of miniemulsion polymerization of BMA (top) and evolution of molecular weight and dispersity with conversion (bottom). [BMA] / [AAm] = 400 (Run 6, filled pentagons), [BMA] / [AAm] = 400 with additional initiator ([VA-086] / [AAm] = 0.25) (Run 9, empty pentagons), [BMA] / [AAm] = 400 with added ascorbic acid (Run 10, half filled pentagons), [BMA] / [AAm] = 400 at pH 4.5 (Run 11, cross filled pentagons).
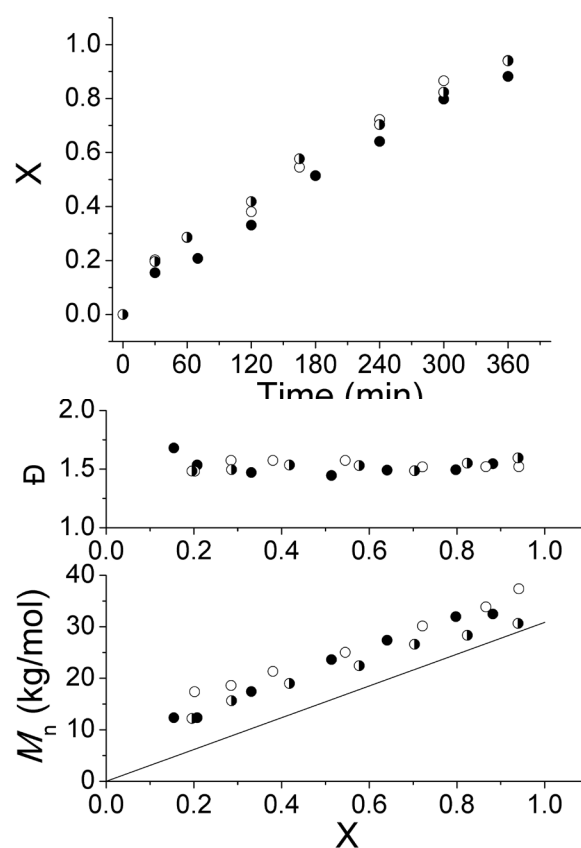

Figure 5 Effect of solids content on kinetics of miniemulsion polymerization of BMA (top) and evolution of molecular weight and dispersity with conversion (bottom). [BMA] / [AAm] = 200, 21 % solids (Run 2, filled circle), 42 % solids (Run 7, empty circles) and 52% solids (Run 8, half filled circles).

One advantage of polymerizations in dispersed media is that they can be conducted at reasonably high solids content without experiencing any significant increase in viscosity. However, it has been extensively reported that the use of RDRP leads to issues with colloidal stability that typically limit the solids content to around 25 wt%.[25] The potential of the present system for the preparation of high solids content latexes was explored by conducting reactions at 42 and 52 wt% monomer (Runs 7 and 8), which represents the upper limit of solids content reported in literature. The evolutions of conversion with time and of molecular weight with conversion were identical in all cases, highlighting the potential to successfully conduct the reactions at high solids content (see Figure 5). In all cases the viscosity of the latexes was moderate, increasing from 2.1 mPa.s for the 21 wt% latex (Run 2), to 4.1 mPa.s for the 42 wt% latex (Run 7), to 15.2 mPa.s for the highest solids content latex (Run 8).

Analysis of the colloidal stability of the initial miniemulsion having 52 % solids content (Run 8) by backscattering measurements showed that in the absence of polymerization the miniemulsion is stable for the duration of the reaction (see Figure S5). In addition, the final polymerized miniemulsions did not contain any significant amount of coagulum and the particle size was similar to that of the initial miniemulsion, suggesting good colloidal stability throughout the reaction. In the case of the reaction conducted at highest solids content (Run 8) the average particle size increased during the reaction before decreasing again (see Figure 6). The cause of this increase was the presence of a small population of micron-sized droplets that appeared due to some limited coalescence of droplets at the high solids contents used (see Figure S6). Although the number of these micron-sized droplets was small, they scattered light more efficiently and led to a distorted particle size when measured by light scattering techniques. Above X ≈ 0.5 the small population of monomer droplets disappeared, with the monomer being absorbed by the particles, leading to a lowering of the particle size as measured by dynamic light scattering.
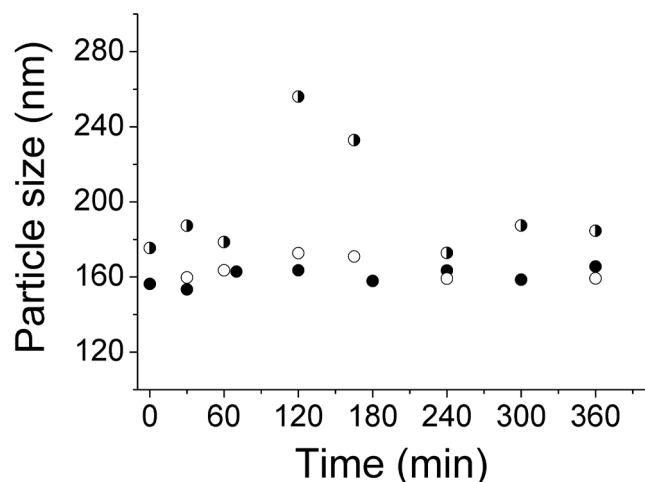
Figure 6 Effect of solids content on evolution of *z*-average particle size with time. [BMA] / [AAm] = 200, 21 % solids (Run 2, filled circle), 42 % solids (Run 7, empty circles) and 52% solids (Run 8, half filled circles).

Figure 7 Molecular weight distribution of poly(butyl methacrylate) synthesized according to Table 2 (dashed black line) and the same polymer after chain extension with benzyl methacrylate (solid red line).

The possibility to synthesize block copolymers was explored by chain extension of a poly(butyl methacrylate) seed latex with benzyl methacrylate. A 10 wt% poly(butyl methacrylate) latex was prepared by batch nitroxide mediated miniemulsion polymerization obtaining a stable dispersion with particle size of 160 nm (X = 0.88, M_n = 37700 g/mol, Đ = 1.47). Benzyl methacrylate was added as a single shot to give a BMA:BzMA weight ratio of 1:1. After 5 h the conversion of the reaction reached 57 % (M_n = 54200 g/mol, Đ = 1.52) and the shift in the molecular weight distribution indicated successful chain extension (see Figure 7). Confirmation of the chain extension process could be observed by comparison of the molecular weight distribution obtained using a UV detector (which only sees those chains containing benzyl methacrylate) and a differential refractive index detector (see Figure S7). The possibility of synthesizing methacrylic block copolymers in dispersed media opens up a wide range of potential applications, particularly in areas where polymers are applied in waterborne dispersions (*e.g.* coatings, adhesives), without the problems typically experienced by other RDRP systems, such as coloration and toxicity.
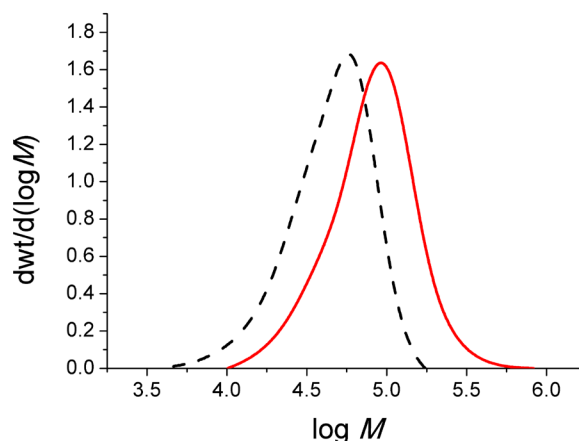
Conclusions

In conclusion, the nitroxide mediated miniemulsion polymerization of butyl methacrylate using the alkoxyamine 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenyl-propanenitrile has been demonstrated. The reaction proceeds to high conversion within a relatively short timescale and solids contents up to 52 wt% yielded stable dispersions. By addition of either an additional radical source, a nitroxide scavenger, or by conducting the polymerization at low pH, the limited conversion that is experience in bulk polymerization when targeting higher molecular weights can be overcome in miniemulsion. The preservation of the nitroxide chain end was confirmed by chain extensions with benzyl methacrylate and demonstrated the possibility for the controlled synthesis of block-copolymers by nitroxide mediated polymerization in dispersed media.

Acknowledgements

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